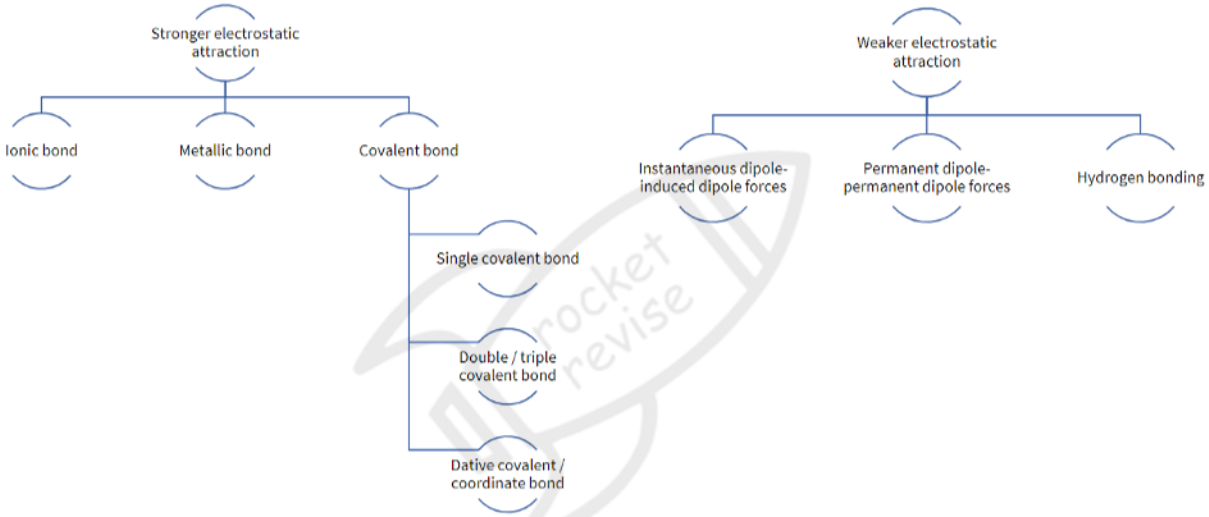
www.RocketRevise.com

CHAPTER 3: CHEMICAL BONDING

Definitions:

- **Ionic bond**: the electrostatic attraction n between oppositely charged ions (cations and anions)
- **Metallic bond**: the electrostatic attraction between cations and delocalized electrons
- **Covalent bond**: the electrostatic attraction between the nuclei of two atoms and a shared pair of electrons
- **Co-ordinate/ dative covalent bond**: the sharing of a pair of electrons between two atoms where both the electrons in the bond come from the same atom
- **Electronegativity**: the power of an atom that is covalently bonded to another atom to attract the bonding pair of electrons to itself
- **Bond energy**: the energy required to break one mole of that bond in a molecule that is in the gaseous state

RocketRevise



Metallic bonds:

- Definition: the electrostatic attraction between cations and delocalized electrons
- This electrostatic attraction acts in all directions

Properties of metals:

- High melting point
    - Metals have high melting and boiling point
        - A lot of energy is required to weaken the strong attractive forces between the metal ions and the delocalized electrons
    - Strength of metallic bonding increases with:
        - Increasing positive charge on ions in metal lattice
        - Decreasing size of metal ions in the lattice
        - Increasing number of mobile electrons per atom

www.RocketRevise.com

www.RocketRevise.com

- Electrical conductivity
  - Metals conduct electricity
    - An electric current can flow across a metal because the delocalized electrons (mobile electrons) are free to move
- Heat conductivity
  - Metals conduct heat
    - Thermal energy can be transferred by conduction – vibrations caused by increased kinetic energy is passed on from one metal ion to the next

Ionic bonds:

- **Definition**: the electrostatic attraction between oppositely charged ions (cations and anions)
- Ions are packed in a regular arrangement called a lattice

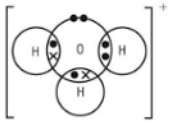
Covalent bonds:

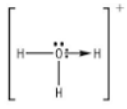
- **Definition**: the electrostatic attraction between the nuclei of two atoms and a shared pair of electrons
- **Bonding pair**: a shared pair of electrons that are involved in covalent bonding
- **Lone pair**: pairs of electrons in the outer shell of an atom that are not involved bonding
- **Single covalent bond**: one shared pair of electrons bonding two atoms together
- **Double covalent bond**: two shared pairs of electrons bonding two atoms together
- **Triple covalent bond**: three shared pairs of electrons bonding two atoms together
- Compounds with coordinate bond, incomplete octet or expanded octet

Coordinate/ dative covalent bond:

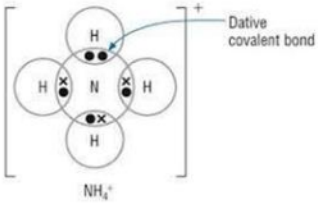
- A type of covalent bond where electrons are shared, however, both bonding electrons come from a lone pair from one atom

H_3O^+



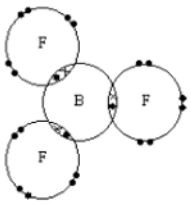


Ammonium ion, NH_4^+

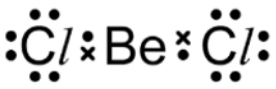


Molecules with incomplete octet:

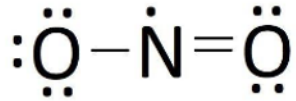
Boron trifluoride, BF_3



$BeCl_2$



NO_2



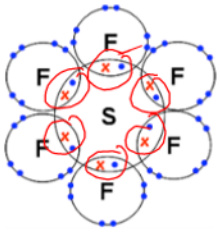
www.RocketRevise.com

www.RocketRevise.com

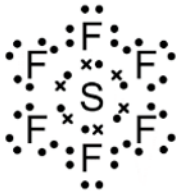
www.RocketRevise.com

Molecules with expanded octet:

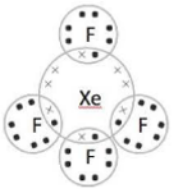
Sulfur hexafluoride, SF_6



Phosphorus pentafluoride, PF_5



Xenon tetrafluoride, XeF_4

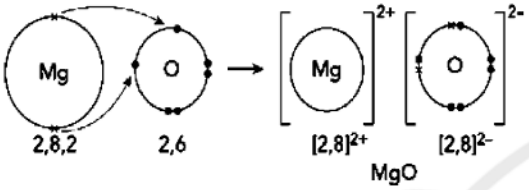


Dot-and-cross diagrams:

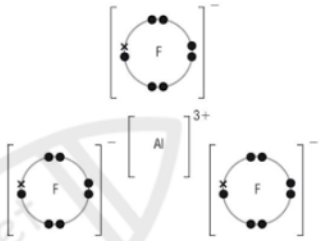
- A dot-and-cross diagram shows:
  - The outer electron shells only
  - The charge of the ion is spread evenly, by using square brackets
  - The charge on each ion, written at the top right-hand corner

RocketRevise

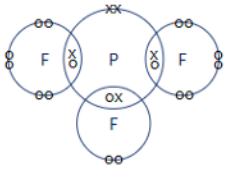
Magnesium oxide



Ionic compounds



Covalent compounds



Molecular orbitals and orbital hybridization:

- **Molecular orbital**: a combined orbital formed by two atomic orbitals overlapping to form a covalent bond
- Recall: An orbital is the region in space where electrons are most likely to be found
- There are 2 ways to describe the type of orbital overlap in covalent bonds:
  - Sigma bond
  - Pi bond

Pauli exclusion principle:

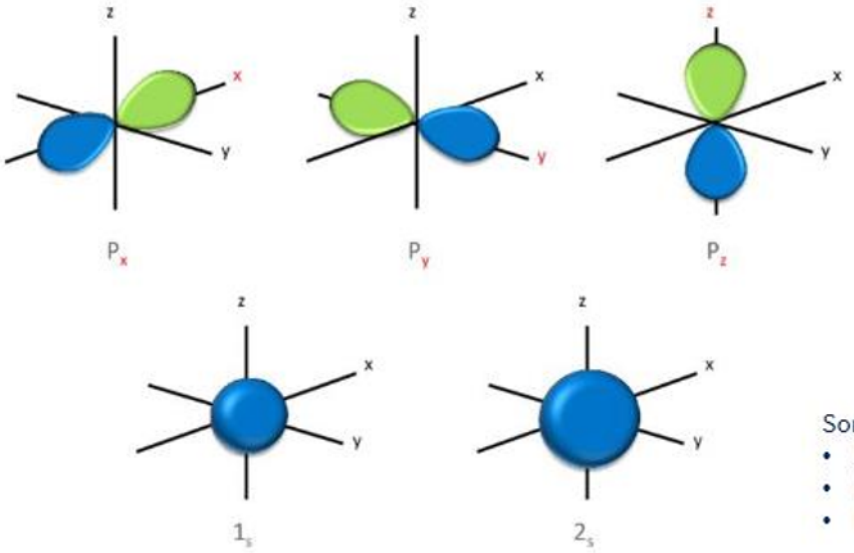
- Pauli exclusion principle requires that the maximum number of electrons in an orbital to be two
- The two electrons in an orbital is of opposite spin

www.RocketRevise.com

www.RocketRevise.com

www.RocketRevise.com

Shapes of atomic orbitals:



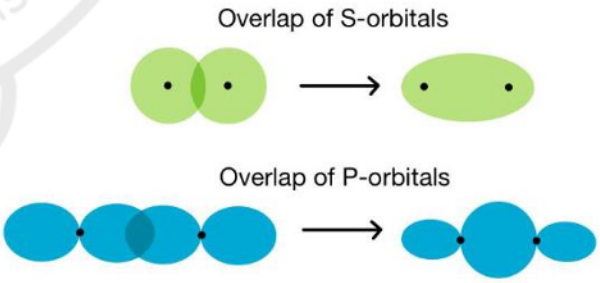
RocketRevise

Some characteristics of an orbital:

- Shape
- Orientation or direction
- Energy

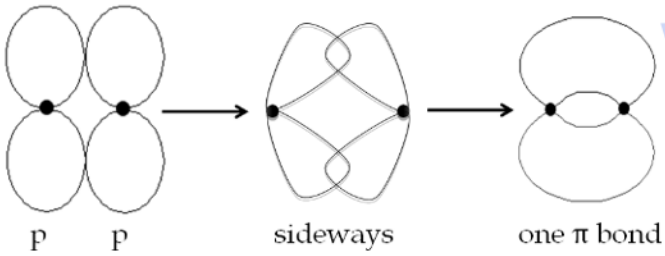
Sigma (σ) bonds:

- Sigma bonds are covalent bonds
- It involves the end-to-end overlapping of an atomic orbital from one atom to another end of an atomic orbital from another atom
- The electron density at the overlapping area would be the greatest



Pi (π) bonds:

- Pi bonds are also covalent bonds
- It involves the side-by-side overlapping of two p orbitals
- Pi bonds are weaker than sigma bond



The 2 electrons in the pi bond may be found in either the upper or lower lobe of the molecular orbital

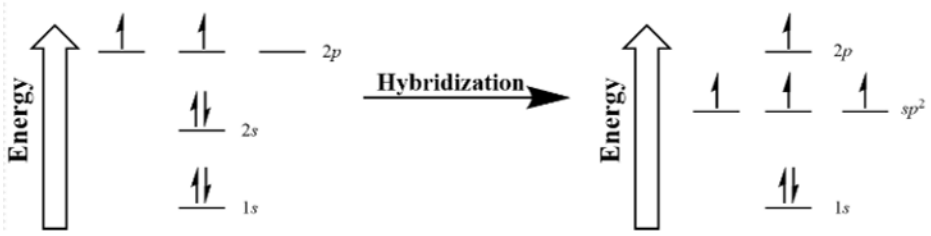
www.RocketRevise.com

www.RocketRevise.com

www.RocketRevise.com

Orbital hybridisation:

- Each atomic orbital which will participate in a covalent bond needs to be singly occupied (one electron in an orbital)
- E.g. of C atom form 4 bonds

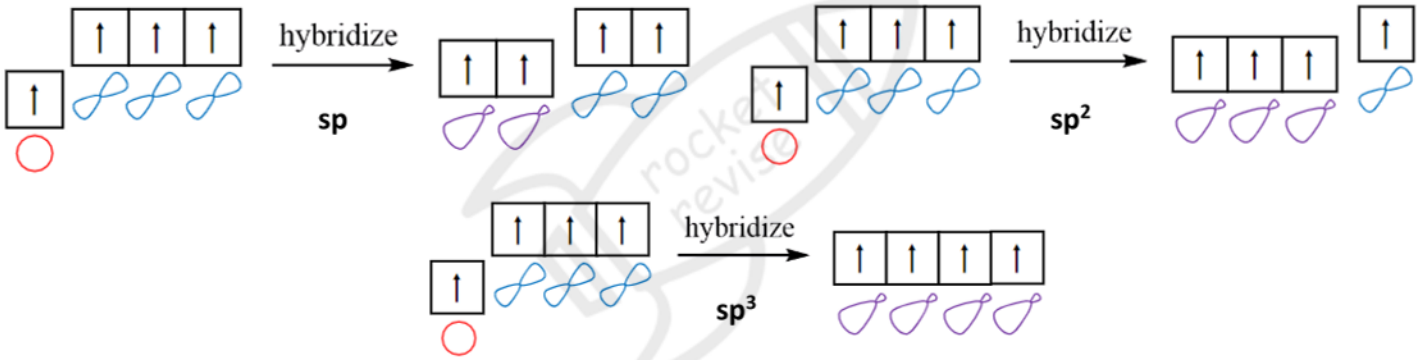


Energy level diagram of a C atom

Energy level diagram of a hybridized C atom

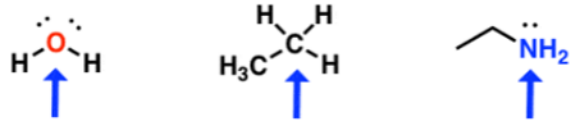
RocketRevise

Hybridisation	Atomic orbitals	Hybrid orbitals	Unhybridised orbitals	Bond angle
sp	s + p	sp + sp	p + p	180°
sp^2	s + p + p	$sp^2 + sp^2 + sp^2$	p	120°
sp^3	s + p + p + p	$sp^3 + sp^3 + sp^3 + sp^3$	-	109.5°



Determining the hybridization of an atom:

the indicated atoms are sp^3 hybridized



2 attached atoms	4 attached atoms	3 attached atoms
+ 2 lone pairs	+ 0 lone pairs	+ 1 lone pair
4	4	4

www.RocketRevise.com

www.RocketRevise.com

www.RocketRevise.com

Summary (orbital hybridization):

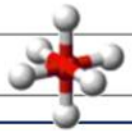
- All single bonds are σ bonds (direct overlap of orbitals)
- π bonds occur in double and triple bonds (sideways overlap of p orbitals)
- Hybridisation can occur in atoms other than C also
- Determine sp, sp^2 or sp^3:
    - sp don't have pi bond
    - sp^2 have one pi bond
    - sp^3 have two pi bond

VSEPR Theory:

RocketRevise

- The shape of a molecules can be deduced using this theory, with the most stable shape being the one with the least repulsion between bonding and lone pairs of electrons

Electron pair geometry:

Number of electron pairs	Electron pair geometry	Shape	Bond angle
1	Linear		180°
2	Linear		180°
3	Trigonal planar		120°
4	Tetrahedral		109.5°
5	Trigonal bipyramid		90, 120°
6	Octahedral		90°

Number of electron pairs	Electron pair geometry	Number of lone pairs	Molecular geometry	Example
2	Linear	0	Linear	CO_2
3	Trigonal planar	0	Trigonal planar	BF_3
4	Tetrahedral	0	Tetrahedral	CH_4
		1	Pyramidal	NH_3
		2	Bent / non-linear	H_2O
5	Trigonal bipyramid	0	Trigonal bipyramid	PF_5
		1	See-saw	SeF_4
6	Octahedral	0	Octahedral	SF_6
		1	Square pyramidal	ClF_5
		2	Square planar	XeF_4

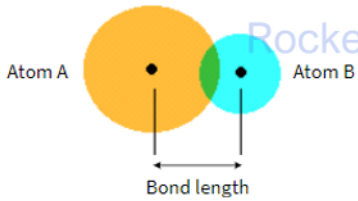
www.RocketRevise.com

www.RocketRevise.com

www.RocketRevise.com

Bond energy and bond strength:

- Bond energy of a bond is the energy required to break one mole of that bond (i.e., to separate the atoms that constitute the bond) in a molecule that is in the gaseous state
- Pi bond is weaker than a sigma bond (when comparing the same atoms)
- Bond length:
    - Bond length is the internuclear distance between two atoms in a covalent bond
    - Atoms with larger radii produces molecules with greater bond length because the valence electrons are further away from the nucleus
    - A shorter bond length indicates a stronger bond due to greater electrostatic attraction between the two atoms



Electronegativity and bond polarity:

- **Electronegativity:** the power of an atom (that is covalently bonded to another atom) to attract the bonding pair of electrons to itself.
- **Bond polarity:** the partial separation of charge when two different atoms are joined by a covalent bond, resulting in an unequal sharing for the bonding pair of electrons

Factors influencing electronegativity:

- **Nuclear charge:**
    - Atoms in the same period with greater nuclear charge are more likely to attract the bonding pair of electrons
- **Atomic radius:**
    - going down the group, atoms become less likely to attract the bonding pair of electrons
- **Shielding:**
    - The greater the shielding effect, the atom becomes less likely to attract the bonding electrons

www.RocketRevise.com

www.RocketRevise.com

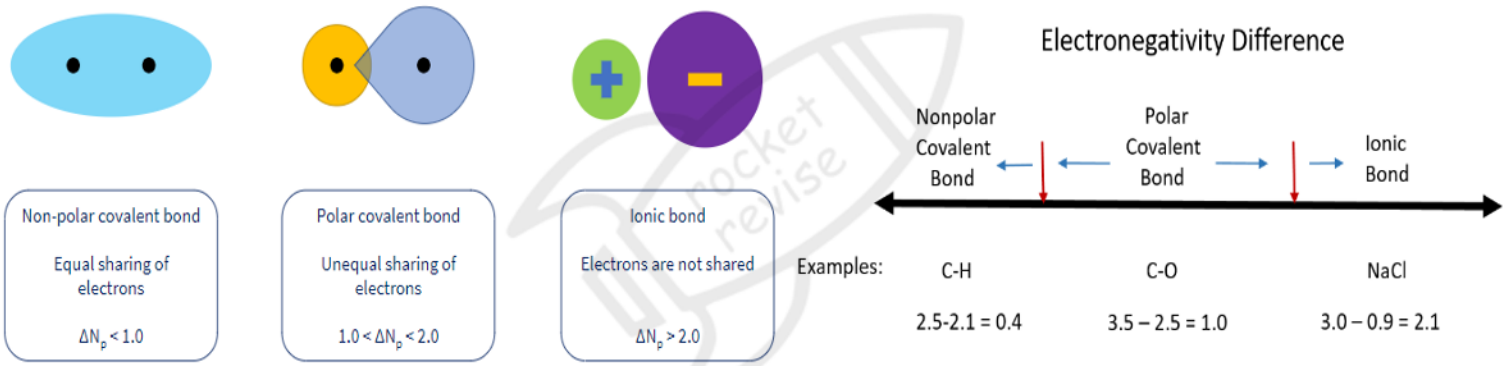
www.RocketRevise.com

Covalent bond:

- **Pure covalent bond:** both atoms in a covalent bond have equal or similar electronegativities
  - Electron distribution is equal between the atoms
  - There is no separation of charge between atoms
  - E.g. Cl_2, H_2
- **Polar covalent bond:** two (bonded) atoms are partially charged – one atom is slightly positive and the other slightly negative
  - Electron distribution is permanently asymmetric/ unequal
  - There is a separation of charge between atoms
  - The bond has a dipole
  - E.g. hydrogen chloride, HCl

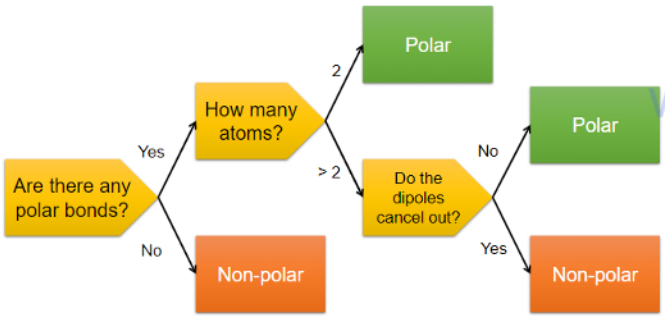
RocketRevise

Comparison between non-polar, polar and ionic bonds:



Polarity in molecules:

- The overall dipole of a molecule depends on its shape and electron distribution
- Dipole moments are vector quantities
- Depending on the relative angles between the bonds, the individual bond dipoles can either reinforce or cancel each other out



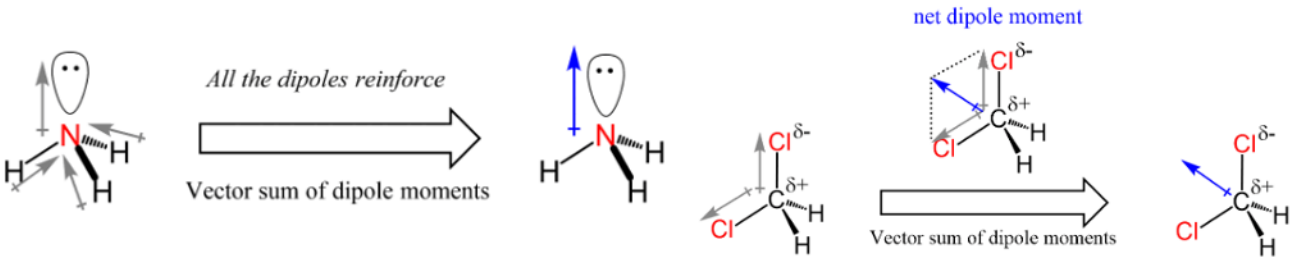
www.RocketRevise.com

www.RocketRevise.com

www.RocketRevise.com

Dipole moment of molecules:

- The dipole moment of a molecule is the vector sum of the dipole moments of all the bonds
- A molecule with net dipole moment (non-zero) is said to be polar



RocketRevise

Bond polarity influences chemical reactivity:

- Many chemical reactions begin when a reagent attacks one of the electrically charged ends of a polar molecule

Intermolecular forces (IMFs):

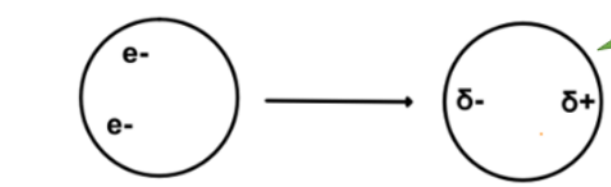
- Exist between discrete covalent molecules
- IMFs are due to formation of temporary and/ or permanent dipoles
- **1. Instantaneous dipole-induced dipole forces:** attractive intermolecular forces caused by temporary instantaneous dipoles in molecules
    - Observed in all (polar and non-polar) molecules
    - Strength depends on number of electrons and size
- **2. Permanent dipole-permanent dipole forces:** attractive intermolecular forces caused by permanent dipoles in molecules
    - Observed in polar molecules
    - Strength depends on charge (electronegativity difference)

www.RocketRevise.com

www.RocketRevise.com

www.RocketRevise.com

- **3. Hydrogen bonding**
  - Observed for H bonded to F, O or N
  - Strongest amongst the intermolecular forces



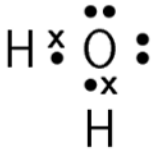
Uneven distribution of electrons in an atom occurs randomly

- The electron cloud is **polarizable** – can be distorted
- Polarisability increases with atomic size

Structures in covalent compounds:

RocketRevise

- Substance that contain covalent bonds may form either:
  - Simple discrete molecules
  - Giant molecular structure (as known as Macromolecular structure)



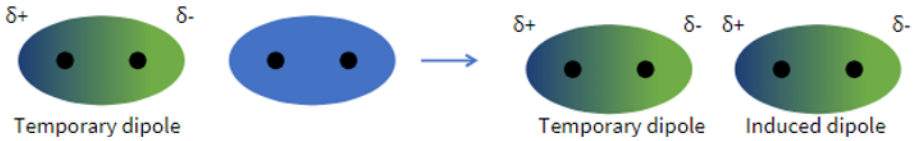
If I can draw a finite dot and cross diagram showing sharing of electrons, that substance will exist as a simple discrete molecule.

The dot and cross diagram of carbon atoms in diamonds may continue in an infinite manner. Diamonds exist as a **giant molecular lattice.**

Instantaneous dipole-induced dipole forces:

- A non-polar molecule may form a temporary dipole force randomly

- This temporary dipole force may induce neighboring molecules to form dipoles also



Temporary dipole — Temporary dipole — Induced dipole

www.RocketRevise.com

- Strength of id-id forces depends on number of electrons, size and contact points between molecules
  - **Number of electrons and size:** e.g. Cl_2 vaporizes around -35°C, Br_2 vaporizes around 59°C, I_2 vaporized around 184°C.
  - **Contact points between molecules:** strength of id-id forces increases with higher number of contact points

www.RocketRevise.com

www.RocketRevise.com

- Explaining molecular packing:

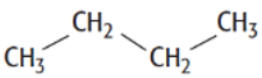
Linear molecules have greater number of contact points between molecules → higher boiling/melting point

Branched molecules have fewer number of contact points between molecules → lower boiling/melting point

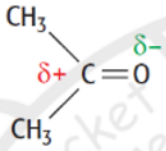
RocketRevise

Permanent dipole-permanent dipole forces:

- Attractive forces between the δ+ charge on one molecule and the δ- charge on another molecule – both molecules have permanent dipoles
- For small molecules with the same number of electrons, pd-pd forces are often stronger than id-id forces



Butane (M_r = 58)
Boiling point 0 °C
Predominant IMF: id-id forces



Propanone (M_r = 58)
Boiling point 56 °C
Predominant IMF: pd-pd forces

Melting points of Halogens vs Hydrogen halides:

Temporary-induced dipole

F_2
Cl_2
Br_2
I_2

Melting point ↑
- No. of electrons ↑ (polarizability ↑)
- Id-id force ↑

Permanent dipole

HF Hydrogen bonding
HCl
HBr
HI

Melting point ↑ from HCl to HI
- Pd-pd force ↓ (less polar)
- Id-id force ↑

www.RocketRevise.com

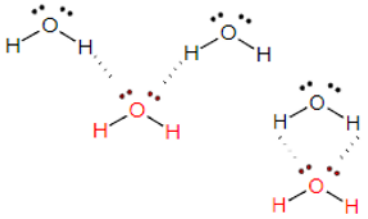
www.RocketRevise.com

www.RocketRevise.com

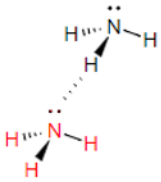
Hydrogen bonding:

- Hydrides of period 2 elements have unusually high boiling points
- HF has an extraordinarily high boiling point
- Criteria for hydrogen bonding:
    - One molecule containing a H atom covalently bonded to F, O or N
    - A second molecule containing F, O or N atom with an available lone pair of electrons

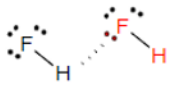
Number of hydrogen bonds per molecule:



Water molecules form an average of two hydrogen bonds per molecule



Ammonia molecules form an average of one hydrogen bond per molecule



HF molecules form an average of one hydrogen bond per molecule

RocketRevise

Strength of hydrogen bonding:

- Hydrogen bonds are a special case of permanent dipole – permanent dipole forces
- The hydrogen bond is typically stronger than dipole-dipole force and temporary-induced dipole forces

Effects of hydrogen bonding:

- H_2O has 2 H bonds per molecule, hence
    - Higher boiling point than NH_3 and HF
    - High viscosity (more fluid) compared to molecules of similar M_r
    - Ice is less dense than water
        - H_2O arranged in a rigid lattice in ice
        - Less densely packed compared to water
- Other effects:
    - Surface tension
        - Attractive forces of molecules at the surface of a liquid that allows it to resist an external force and reduce its surface area

www.RocketRevise.com

www.RocketRevise.com

www.RocketRevise.com

- Solubility
  - Polar compounds dissolve in polar solvents
    - When a compound dissolves in water
    - IMF between solute breaks, and new IMF formed between water molecules and solute
  - Non-polar compounds dissolve in non-polar solvents
    - Oil (non-polar) do not dissolve in water

Solubility of compounds in water:

RocketRevise

- A compound generally dissolves in water if
  - The compound is ionic e.g. NaCl
  - The predominant IMF is permanent dipole-permanent dipole forces. E.g. HCl
  - The compound can form hydrogen bonds e.g. CH_3CH_2OH
- Some ionic compounds are sparingly soluble (insoluble) in water
  - E.g. $Mg(OH)_2$, $CaCO_3$

Summary of intermolecular forces:

Intermolecular force	Type of molecules	Examples
Instantaneous dipole-induced dipole (id-id)	Non-polar OR Polar molecule with a large non-polar group such that the molecule is predominantly non-polar	Noble gases, hydrocarbons, H_2 N_2, CO_2, $AlCl_3$, $SiCl_4$, PF_5, SF_6, polymers
Permanent dipole-permanent dipole	polar	HCl, SO_2, NH_3, H_2S
Hydrogen bond (H-bond)	Contains H-F, H-O or H-N bonds Amides (A2 syllabus)	H_2O, NH_3, HF, alcohols, amines

*a common misconception:
permanent dipole forces are **always** stronger than instantaneous dipole-induced dipole forces

In reality: id-id forces may be stronger than pd-pd forces. id-id forces become stronger when the size of the atom/molecule becomes larger

Exam answering tip:

www.RocketRevise.com

Key differences in IMF taught in O Levels/SPM and A Levels:

O Level / SPM	A Level
Weak intermolecular forces OR Weak VDW forces exist between simple covalent molecules	There are 3 types of IMFs: Instantaneous/temporary dipole-induced dipole Permanent dipole-permanent dipole Hydrogen bond

www.RocketRevise.com